

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11

Publication number:

**0 172 957
A1**

12

EUROPEAN PATENT APPLICATION

21

Application number: 84305884.3

51

Int. Cl.⁴: **C 08 L 61/06, C 08 K 7/02,
C 08 J 5/04, F 02 K 9/34**

22

Date of filing: 29.08.84

43

Date of publication of application: 05.03.86
Bulletin 86/10

71

Applicant: **HERCULES INCORPORATED**, Hercules
Plaza, Wilmington Delaware 19894 (US)

72

Inventor: **Herring, Liles Gall**, 810 Fairway Road
Woodway, Waco Texas 76710 (US)

84

Designated Contracting States: **DE FR GB**

74

Representative: **De Minville-Devaux, Ian Benedict
Peter et al, CARPMAELS & RANSFORD** 43, Bloomsbury
Square, London WC1A 2RA (GB)

54

Phenolic blast tube insulators for rocket motors.

57

Phenolic insulators for blast tubes of rocket motors are disclosed. The insulators are rigid, low density bodies comprising 100 parts by weight crosslinked phenolic resin in which are dispersed finely divided inorganic particulate and fibrous reinforcement selected from carbon fiber, polyaramide pulp and combinations thereof. Compounding these rigid bodies is also disclosed, the compounding including forming a molding crumb containing the aforesaid ingredients.

EP 0 172 957 A1

This invention relates to thermal heat shields or insulators for rocket motors, particularly for blast tubes and blast tube ramp sections, and more particularly to such insulators that are formed of cured phenolic resin in which
5 fibrous reinforcement material is dispersed; and it relates to an improved process for making them.

A blast tube, positioned between the nozzle and propellant sections of tactical rocket motors, is normally a cylindrical conduit of smaller diameter than the motor that
10 conveys the hot combustion products of the propellant to the nozzle. The converging section connecting the rocket motor and the blast tube proper is the blast tube ramp section. The blast tube insulator serves as a liner for the inner
15 surfaces of these parts, to protect them from damage caused by the hot combustion products during the flight of the missile.

A blast tube insulator must have thermal properties, including char rates, that are consistent with its high temperature, erosive environment. Such insulators can be molded
20 from a commercially-available phenolic resin precursor containing 1.27 cm. squares of carbon or silica cloth. However, they are expensive and difficult to process, and they require to be so highly filled with the carbon or silica cloth that they have high densities that unduly increase the
25 inert weight carried by the rockets in which they are installed.

According to the invention, these deficiencies of the commercially-available reinforced materials are overcome by a rigid molded insulator formed from a cured phenolic resin

composition in which fibrous reinforcement material is dispersed, the insulator being characterized in that the fibrous reinforcement material comprises polyaramide pulp or carbon fibers or a combination of said pulp and fibers, and
5 for each 100 parts by weight of cured phenolic resin in the composition, the insulator contains between about 30 and 120 parts by weight of the said material and between about 10 and 60 parts by weight of a finely divided inorganic particulate, and having a density in a range between about 1.14 and 1.495
10 Mg/m^3 100.

Also according to the invention, a method of preparing the blast tube insulator according to the invention, is characterized in that the inorganic particulate is silica, and the phenolic precursor for the cured phenolic resin is
15 admixed with the silica and the fibrous reinforcement in the presence of a solvent for the precursor until a molding crumb having a diameter between about 4 and 8 millimeters results, the crumb is dried by tumbling in dry air and loaded into a mold, sufficient pressure to consolidate the crumb is applied
20 to the crumb in the mold at a temperature between about 93 and 232°C. for a time sufficient to cure the precursor and form the insulator.

By employing relatively inexpensive silica particulate and carbon or polyaramide fibers to replace the more
25 expensive chopped carbon or silica cloths of the commercially reinforced materials, the blast tube insulators according to the invention can be formulated to achieve unexpectedly lower levels of density, without any significant loss in other properties, including char rates. They also eliminate the
30 difficulties involved in handling and chopping such cloths.

The phenolic resin precursor used in making the blast tube insulators of this invention is commercially available. The preferred phenolic resin materials are those sold as Resinox^R phenolics by Monsanto Chemical Company. Other
35 phenolic resin materials suitable for this invention include those, which like the Resinox^R materials, cure by crosslinking a phenolic compound with formaldehyde or other

such aldehyde or ketone acting as a difunctional linking moiety. The difunctional linking moiety links the phenolic groups in the phenolic resin materials to provide the cross-linking for the insulators. Hexamethylenetetramine is
5 desirably included in the phenolic resin material for producing the formaldehyde for the crosslinking reaction.

For certain applications, particularly for insulating blast tube ramp sections, the phenolic resin precursor desirably contains up to 100 parts by weight per hundred
10 parts by weight of the phenolic resin material of a cross-linked elastomeric polymer, such as one of the synthetic rubbers: for instance, ethylene propylene diene monomer (EPDM), polyurethane, chlorosulphonated polyethylene, and polychloroprene. These rubbery polymers are crosslinked
15 by peroxy or other crosslinking agents included in the insulating materials.

(The expression "phr" is used in this description to mean "parts by weight per hundred parts by weight of the phenolic resin material").

20 The finely divided, inorganic particulate is included in the blast tube insulators in a range between about 10-60 phr, preferably in a range between about 15-50 phr. The inorganic filler preferably has a particle size of between about 10 and 50 microns (average diameter), and more preferably between
25 about 20 and 40 microns in average diameter. The preferred inorganic filler is silica, particularly hydrated silica formed by precipitation. Hil Sil^R silica available from Harwick Chemical is the preferred inorganic particulate for use in the insulators of this invention.

30 Other inorganic particulates can be used in accordance with this invention and include siliceous materials such as mica, glass, quartz and combinations thereof which may be used alone or together with the silica. Preferably, however, the inorganic particulate consists essentially of silica,
35 particularly hydrated silica of the particle size identified above.

The polyaramide pulp suitable for use in this invention is commercially available, being sold for example, by E. I. duPont as Kevlar^R aramide pulp fiber. The polyaramide pulp preferably is a short, highly fibrillated fiber in which the
 5 fibrillation is resultant of axially oriented, strong crystallites that are less strongly bonded transversely. Fibrillation of the pulp fiber leads to length to diameter ratios (L/D) of over 500. An important advantage of these polyaramide pulps is their very high decomposition tempera-
 10 tures ranging above about 400°C. In addition, these polyaramide pulps are low density and decompose into a strong, adherent char.

The preferred polyaramide pulps have physical properties as set forth in Table I:

15

Table I

	Tensile Strength	
	KPa x 10 ³	3000 - 4000
	Tensile Modulus	
	KPa x 10 ⁶	75 - 100
20	Elongation	
	%	3 - 5
	Density	
	g/cc	1.4 - 1.5
	Filament Dia.	
25	um	10 - 14
	Degradation Temp.	400 - 600°C.
	Thermal Expansion Coefficient	-2 x 10 ⁻⁶ /°C.

Further characterization of suitable polyaramide pulps currently available for use in this invention are set forth
 30 in Table II below:

Table II

	A*	B*	C*
+14 Mesh	16 \pm 5*	4 \pm 2	4 \pm 2
-14 +30 Mesh	22 \pm 5	17 \pm 3	17 \pm 3
5 -30 +50 Mesh	25 \pm 3	33 \pm 5	33 \pm 5
-50 +100 Mesh	19 \pm 4	26 \pm 2	26 \pm 2
-100 Mesh	17 \pm 5	20 \pm 4	20 \pm 4
Nominal Average Length	4mm	2mm	2mm

*Kevlar pulps sold by Dupont as Long Wet Lap, Merge 6F204; Short Wet Lap Merge 6F205; and Dry Pulp Merge 6F218, respectively.

The dry pulp C is preferred for this invention. Drying of the other pulps B and C prior to compounding enhances their utility for use in this invention. The above characterizations of suitable polyaramide pulps is for exemplification only; other similar aromatic polyamides including, for example, polyaramide fibers can be suitably employed in this invention.

The carbon fiber useful as the fibrous reinforcement of the insulating materials is commercially available. The length of the fiber is preferably between about 2 and 10 millimeters with diameters between about 4 and 16 microns. The carbon fiber can be made by heating polyacrylonitrile or pitch filaments for a time sufficient to reduce the fiber to highly carbonized form followed by chopping the filaments into desired form.

Exemplary characteristics for carbon fiber suitable for use in this invention and made from polyacrylonitrile precursor fiber are set forth below in Table III:

Table III

	Tensile strength	2,480 MPa
	Tensile modulus	206 GOa
	Ultimate elongation	1.2%
5	Density	1.77 g/cm ³
	Size cointent (% by weight)	7% max.
	Bulk density	280 g/l
	Filament diameter	8 microns
	Filament shape	Round

10 The blast tube insulators of this invention can be made by blending the aforescribed ingredients in dry form followed by introducing the dry blend into a mold. However, use of a dry blend of particulate can result in ingredient separation during handling and storage. Accordingly, the preferred compounding procedure uses an initial dry blending of the

15 insoluble ingredients followed by addition of the phenolic resin materials dissolved in solvent. Use of a vertical planetary mixer device is preferred for this compounding. The addition of dissolved phenolic resin materials to the admixed particles over the period of mixing permits the phenolic resin materials to deposit on the inorganic and organic

20 particulates in the mixture. These particulates, carrying the plated out phenolic resin material, tend to agglomerate during mixing into small clumps. It is preferred that the clumps or crumbs are kept within a particle size of between

25 about 4 and 8 millimeters.

Exemplary solvents for this mixing procedure are low boiling polar solvents such as methylethylketone, acetone, and ethyl alcohol. After the crumb is formed, it is tumbled

30 in dry air (temperature e.g. 16-27°C. to remove the solvent.

Curing of the blast tube insulators is under pressure (e.g. 500-2000 psig) at temperatures ranging between 93 and 232°C. A preferred cure cycle is cure at a temperature of between about 93 and 107°C. for between 1-3 hours followed by

cure at temperatures in a range between 149 and 204°C. for 1-3 hours. The cured insulators are preferably cooled before release of pressure. The aforementioned dual heating procedure followed by cooling in the mold reduces the probability of cracking during molding of the insulators.

The blast tube insulators of this invention have densities between about 1.439 and 1.495 Mg/m³. This density is lower (e.g. 16%) than certain conventional phenolic blast tube insulators containing chopped carbon or silica cloth. The lower density coupled with comparable char rate performance leads to better insulators for the blast tubes.

Exemplary formulations for the blast tube insulators of this invention are set forth in Tables A and B below.

Table A

Ingredient	Parts by Weight
Phenolic Resin Materials	100
Carbon Fiber	40-120
Silica Particulate	10-30

Table B

Ingredient	Parts by Weight
Phenolic Resin Materials	100
Polyaramide Pulp	40-120
Silica Particulate	30-50

The following examples illustrate this invention but are not meant as a limitation thereof. In these examples, all parts are parts by weight unless specifically noted otherwise. As used in these examples, "Erosion Rate" is defined as the thickness of the insulator before test less the thickness after the test divided by action time where action time is

the time between when the motor starts to exhaust at 7 kg./cm² and when the exhaust decreases to 7 kg./cm². "Char Rate" is defined as the insulator thickness after the test minus the thickness after removal of char divided by the
5 action time. "Decomposition Rate" is defined as the insulator thickness before the test minus the thickness after char removal divided by the action time. Erosion rate values derived from an accumulation rather than a removal of
10 material during the test (such that the subtraction noted above would not lead to a positive number), are preceded by a plus (+) sign.

Example 1

Set forth in Table 1 below is a comparison between blast tube insulators of this invention (formulations A, B, C) and
15 those of the prior art (D, E). As can be seen from data of this Table 1, the insulators of this invention can be lower in density and still have properties in two-inch rocket motor test firings that are comparable to those of insulators made from commercially-available material. All the insulators (A,
20 B, C) of this invention in Table 1 were prepared by blending of the ingredients followed by molding at 10.34 - 13.79 Pa for 2 - 3 hours at about 177°C.

0172957

TABLE 1

<u>Ingredient, phr</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D(a)</u>	<u>E(a)</u>
Phenolic Resin (b)	100.0	100.0	100.0		
Hydrated Silica, precipitated (c)	20.0	20.0	20.0		
Carbon Fiber (1.55 cm.) (d)	50.0				
Carbon Fiber (e)		50.0			
Polyaramide Pulp (f)			100.0		
Silica Cloth, Chopped (1.27 cm. sq.)				400.0	
Phenolic Resin (g)				100.0	
Phenolic Resin (h)					100.0
Carbon Cloth, Chopped (1.27 cm. sq.)					194.1
Erosion Data @ Mass Flux of approx. .13 kg./sec.-cm. ² (i)					
Erosion Rate, mm./sec.	.051	.025	.038	+.152	.127
Decomposition Rate, mm./sec	.356	.114	.178	.737	.254
Char Rate, mm./sec	.279	.0762	.1397	.9144	.127
Density, Mg/m ³	<u>1.484</u>	<u>1.475</u>	<u>1.448</u>	<u>1.772</u>	<u>1.500</u>

- (a) Product of Fiberite Co. MX2646; MX4926
- (b) Resinox^R 755 product of Monsanto
- (c) Hisil^R product of P.P.G. Industries
- (d) Magnamite^R 1810 as product of Hercules Incorporated, passed through roll mills.
- (e) Celion C-6 product of Celanese
- (f) Kevlar^R 29 pulp, type 979, merge 6F 218
- (g) Polyamide modified phenolic resin
- (h) Phenolic Resin, MIL-R-9299, Type II
- (i) Data from two-inch motor firings

As can be seen from the data on Table 1, the insulators of this invention (formulations A, B, C) have erosion, decomposition and char rates comparable to those of the prior art (formulations D, E). Since the density of the insulator of this invention is lower than the insulators made from commercially-available material, as can also be seen from Table 2, a smaller weight of insulation can be used, or a greater amount of low density insulation can be used to yield better performance at the same weight level.

10

Example 2

Set forth in Table 2 is a summary of data obtained in firing subscale rocket motors that were insulated in accordance with this invention (2A - 2J) or with commercially-available material (MX2646, 4926). Table 3 shows the formulations of the blast tube insulators of Table 2. "Erosion Rate" and "Decomposition Rate" are defined as indicated above, as insulator thickness differences before and after testing divided by the action time, and erosion rate values derived from an accumulation rather than a removal of material during the test are preceded by a plus (+) sign.

15

As can be seen from Tables 2 and 3, the blast tube insulators of this invention perform in a manner comparable to the insulators made of commercially-available material.

20

TABLE 2

Formulation No.	Decomposition Rate mm./sec Mass Flux			Erosion Rate mm./sec Mass Flux			Density* Mg/m ³
	<u>Low</u>	<u>Med.</u>	<u>High</u>	<u>Low</u>	<u>Med.</u>	<u>High</u>	
2A	.457	.812	.889	+.102	+.102	.025	1.520

25

	2B	.381	.610	.660	.025	.025	.025	1.448
	2C	.305	.584	.584	+.711	+.025	.076	1.140
	MX-2646	.381	.457	.533	+.381	+.381	+.229	1.772
	2D	.381	.635	.711	+.737	+.102	.025	1.475
5	2E	.330	.813	.838	+.330	+.076	.051	1.575
	2F	.330	.635	.787	+.203	+.025	.279	1.276
	MX-4926	.356	.686	.914	+.178	.025	.102	1.500
	2G	.381	.508	.559	.076	.178	.229	1.357
	2H	.330	.559	.584	.051	.178	.203	1.390
10	2O	.203	.559	.660	.127	.305	.508	1.413
	2J	.914	1.17	1.29	.102	.102	.178	1.672

*Theoretical

TABLE 3

		<u>Phenolic Insulations</u>					
	Ingredients, phr	2D	2A	2E	X02646	MX4926	2B
15	Phenolic Resin ¹	100.0	100.0	100.0	--	--	100.0
	Silica ²	20.0	26.67	40.0	--	--	40.0
	Graphite Fiber ³	50.0	--	--	--	--	--
	Graphite Fiber ⁴	--	66.67	100.0	--	--	--
20	Phenolic Resin						
	(Mil-R-9299, Type II)	--	--	--	100.0 ⁽⁵⁾	100.0	--
	Silica Cloth, Chopped, 1.27 cm. sq.	--	--	--	400.0	--	--
	Carbon Cloth, Chopped 1.27 cm. sq.	--	--	--	--	194.1	--
25	Polyaramide pulp ⁶	--	--	--	--	--	100.0

		<u>Phenolic-Elastomeric Insulations</u>					
		2F	2C	2G	2H	2J	2K
30	Chlorosulfonated poly- ethylene ⁷	80.0	50.0	100.0	100.0	100.0	100.0
	Liquid Polybutadiene ⁸	20.0	30.0	--	--	--	--
	Polyisoprene ⁹	--	20.0	--	--	--	--
	Polyaramide pulp ¹⁰	50.0	50.0	200.0	1250.0	2500.0	--
	Starch	40.0	40.0	40.0	40.0	40.0	40.0

	Magnesia	6.0	2.0	6.0	6.0	6.0	6.0
	Sulfur accelerator ¹¹	2.0	1.0	2.0	2.0	1.0	1.0
	Phenolic resin ¹²	100.0	100.0	200.0	500.0	500.0	500.0
	Peroxy curative ¹³	--	3.75	--	--	--	--
5	Silica ¹⁴			40.0	--	--	--
	Graphite Fiber ¹⁵			--	--	--	2500.0

1. Resinox 755, Monsanto
2. HiSil, Harwick
3. Celion 6, Celanese
- 10 4. Magnamite, Hercules
5. Polyamide modified
6. Kelvar 29, DuPont
7. Hypalon LP 999, DuPont
8. Ricon 150, Colorado Speciality
- 15 9. Natsyn 2200
10. See 6
11. Dipentamethylenethiuriumhexasulfide, DuPont
12. See 1
13. 2,5-dimethyl-2,5di(t-butylperoxy)hexane
- 20 14. See 2
15. Celion 6, Celanese

Example 3

Eighteen-kilogram rocket motors were fabricated for testing the blast tube insulators of the invention. The formulations tested were 2B, 2C, and 2D of Example 2, Tables 2 and 3.

Billets of these formulations 2B, 2C, and 2D were molded. Two billets of each were required for testing: 2.5 inch outside diameter by 5 inch long, and 6.6 inch outside diameter by 2.5 inch long. These billets were compression molded in piston-type molds, then cured at 177°C. Blast tube insulator components were machined from the billets and bonded into the blast tube hardware, including ramp section.

The results of firing eighteen-kilogram motors containing these insulators are shown in Table 4. These results are for four motor firings, 1-4, and show Erosion rate (ER) and Decomposition rate (DR).

5 As can be seen by the results in Table 4, the insulation of this invention performed favorably.

TABLE 4

Location/ Motor No.	Mass Flux $\frac{\text{kg}}{\text{sec-cm}^2}$	Velocity m/sec	2C		2B		2D	
			ER	DR	ER	DR	ER	DR
10 Ramp Section								
Motor No. 1	.0392	.296	.18	.18				
	.0492	36.9	.23	.15				
Motor No. 2	.0372	31.7	.15	.13				
15	.0475	40.2	.15	.15				
Blast Tube								
Motor No. 2	.0584	44.2	.30	.15				
	.1561	118	1.1	1.2				
	.4633	370	2.3	2.3				
20 Motor No. 3	.0555	47.2			.10	.18		
	.1687	145		.08	.33			
	.5062	472			1.3	1.4		
Motor No. 4	.0541	47.9					0	.63
	.1659	147					.13	.66
25	.5941	611					.30	.91

1. A rigid molded insulator suitable for thermally shielding the blast tube of a rocket motor and formed from a cured phenolic resin composition in which is dispersed fibrous reinforcement material, characterized in that the
5 fibrous reinforcement material comprises polyaramide pulp or carbon fibers or a combination of said pulp and fibers, and for each 100 parts by weight of phenolic resin the insulator contains between about 30 and 120 parts by weight of the said reinforcement material and between about 10 and 60 parts by
10 weight of a finely divided inorganic particulate, the insulator having a density between about 1.14 and 1.495 Mg/m^3 .

2. A rigid molded insulator as claimed in claim 1, further characterized in that the fibrous reinforcement
15 comprises polyaramide pulp.

3. A rigid molded insulator as claimed in claim 1 or 2, further characterized in that it contains between about 40 and 80 parts by weight of polyaramide pulp and between about 10 and 30 parts by weight of finely divided inorganic
20 particulate, per hundred parts by weight of the phenolic resin, the insulator having a density between about 1.439 and 1.467 Mg/m^3 .

4. A rigid molded insulator as claimed in claim 1 or 2, further characterized in that it contains between about 80
25 and 120 parts by weight of carbon fibers and between about 30 and 50 parts by weight of finely divided inorganic particulate, per hundred parts by weight of the phenolic resin, the insulator having a density between about 1.467 and 1.495 Mg/m^3 .

5. A rigid molded insulator as claimed in claim 1, further characterized in that it contains between about 40 and 80 parts by weight of carbon fibers that are between about 4 and 8 millimeters long, and between about 10 and 30 parts by weight of a finely divided inorganic particulate, per hundred parts by weight of the phenolic resin.

6. A rigid molded insulator as claimed in any of the preceeding claims, further characterized in that the finely divided inorganic particulate comprises silica.

10 7. A rigid molded insulator as claimed in any of the preceeding claims, further characterized in that the phenolic resin composition contains up to up to 100 parts by weight of a cross-linked elastomeric polymer per hundred parts by weight of the phenolic resin.

15 8. A method of preparing the blast tube insulator as claimed in Claim 5, characterized in that a curable precursor for the cured phenolic resin is admixed with the silica and the fibrous reinforcement in the presence of a solvent for the precursor until a molding crumb having a diameter between
20 about 4 and 8 millimeters results, the crumb is dried by tumbling in dry air and loaded into a mold, sufficient pressure to consolidate the crumb is applied to the crumb in the mold at a temperature between about 93 and 232°C. for a time sufficient to cure the precursor and form the insulator.



European Patent
Office

EUROPEAN SEARCH REPORT

0172957

Application number

EP 84 30 5884

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	CHEMICAL ABSTRACTS, vol. 83, no. 8, 25th August 1975, page 63, no. 60112m, Columbus, Ohio, US; R.W. FARMER: "Extended heating ablation of carbon phenolic and silica phenolic" & GOVT. REP ANNOUNCE. (U.S.) 1975, 75(1), 84	1-8	C 08 L 61/06 C 08 K 7/02 C 08 J 5/04 F 02 K 9/34
A	--- CHEMICAL ABSTRACTS, vol. 93, no. 18, 3rd November 1980, page 27, no. 168971m, Columbus, Ohio, US; C.G. GOETZEL: "High-temperature properties of some reinforced phenolic composites" & HIGH TEMP. - HIGH PRESSURES 1980, 12(2), 131-146	1-8	
A	--- US-A-4 119 036 (M. HAYASHI et al.) * Claims 12,13 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	--- EP-A-0 074 838 (THIOKOL CORP.) * Claims *	1	F 02 K C 08 J C 08 K C 08 L
A	--- GB-A- 757 890 (MICROCELL) -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24-04-1985	Examiner HOFFMANN K.W.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 14.03.90

(71) Application number: 84305884.3

(72) Date of filing: 29.08.84

(51) Int. Cl.⁵: **C 08 L 61/06, C 08 K 7/02,**
C 08 J 5/04, F 02 K 9/34

(54) **Phenolic blast tube insulators for rocket motors.**

(49) Date of publication of application:
05.03.86 Bulletin 86/10

(45) Publication of the grant of the patent:
14.03.90 Bulletin 90/11

(84) Designated Contracting States:
DE FR GB

(56) References cited:
EP-A-0 074 838
GB-A- 757 890
US-A-4 119 036

CHEMICAL ABSTRACTS, vol. 83, no. 8, 25th
August 1975, page 63, no. 60112m, Columbus,
Ohio, US; R.W. FARMER: "Extended heating
ablation of carbon phenolic and silica phenolic"
& GOVT. REP ANNOUNCE. (U.S.) 1975, 75(1), 84

CHEMICAL ABSTRACTS, vol. 93, no. 18, 3rd
November 1980, page 27, no. 168971m,
Columbus, Ohio, US; C.G. GOETZEL: "High-
temperature properties of some reinforced
phenolic composites" & HIGH TEMP. - HIGH
PRESSURES 1980, 12(2), 131-146

(73) Proprietor: **HERCULES INCORPORATED**
Hercules Plaza
Wilmington Delaware 19894 (US)

(72) Inventor: **Herring, Liles Gail**
810 Fairway Road Woodway
Waco Texas 76710 (US)

(74) Representative: **De Minvielle-Devaux, Ian**
Benedict Peter et al
CARPMAELS & RANSFORD 43, Bloomsbury
Square
London WC1A 2RA (GB)

(58) References cited:

The file contains technical information
submitted after the application was filed and
not included in this specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

Description

This invention relates to thermal heat shields or insulators for rocket motors, particularly for blast tubes and blast tube ramp sections, and more particularly to such insulators that are formed of cured phenolic resin in which fibrous reinforcement material is dispersed; and it relates to an improved process for making them.

A blast tube, positioned between the nozzle and propellant sections of tactical rocket motors, is normally a cylindrical conduit of smaller diameter than the motor that conveys the hot combustion products of the propellant to the nozzle. The converging section connecting the rocket motor and the blast tube proper is the blast tube ramp section. The blast tube insulator serves as a liner for the inner surfaces of these parts, to protect them from damage caused by the hot combustion products during the flight of the missile.

A blast tube insulator must have thermal properties, including char rates, that are consistent with its high temperature, erosive environment. Such insulators can be molded from a commercially-available phenolic resin precursor containing 1.27 cm squares of carbon or silica cloth. However, they are expensive and difficult to process, and they require to be so highly filled with the carbon or silica cloth that they have high densities that unduly increase the inert weight carried by the rockets in which they are installed.

According to the invention, these deficiencies of the commercially-available reinforced materials are overcome by a rigid molded insulator formed from a cured phenolic resin composition in which fibrous reinforcement material is dispersed, which fibrous reinforcement material comprises polyaramide pulp or carbon fibers or a combination of said pulp and fibers, and in which for each 100 parts by weight of cured phenolic resin in the composition, the insulator contains between 30 and 120 parts by weight of the said material and between 10 and 60 parts by weight of a finely divided siliceous inorganic particulate, the insulator having a density in a range between 1.14 and 1.495 Mg/m³.

A method of preparing the blast tube insulator according to the invention is characterized in that the phenolic precursor for the cured phenolic resin is admixed with the inorganic particulate, preferably silica, and the fibrous reinforcement in the presence of a solvent for the precursor until a molding crumb having a diameter between 4 and 8 millimeters results, the crumb is dried by tumbling in dry air and loaded into a mold, and sufficient pressure to consolidate the crumb is applied to the crumb in the mold at a temperature between 93 and 232°C for a time sufficient to cure the precursor and form the insulator.

By employing relatively inexpensive silica particulate and carbon or polyaramide fibers to replace the more expensive chopped carbon or silica cloths of the commercially reinforced materials, the blast tube insulators according to the invention can be formulated to achieve unexpectedly lower levels of density, without any significant loss in other properties, including char rates. They also eliminate the difficulties involved in handling and chopping such cloths.

The phenolic resin precursor used in making the blast tube insulators of this invention is commercially available. The preferred phenolic resin materials are those sold as Resinox (registered trade mark) phenolics by Monsanto Chemical Company. Other phenolic resin materials suitable for this invention include those, which like the Resinox materials, cure by crosslinking a phenolic compound with formaldehyde or other such aldehyde or ketone acting as a difunctional linking moiety. The difunctional linking moiety links the phenolic groups in the phenolic resin materials to provide the crosslinking for the insulators. Hexamethylenetetramine is desirably included in the phenolic resin material for producing the formaldehyde for the cross-linking reaction.

For certain applications, particularly for insulating blast tube ramp sections, the phenolic resin precursor desirably contains up to 100 parts by weight per hundred parts by weight of the phenolic resin material of a cross-linked elastomeric polymer, such as one of the synthetic rubbers: for instance, ethylene propylene diene monomer (EPDM), polyurethane, chlorosulphonated polyethylene, and polychloroprene. These rubbery polymers are crosslinked by peroxy or other crosslinking agents included in the insulating materials.

(The expression "phr" is used in this description to mean "parts by weight per hundred parts by weight of the phenolic resin material").

The finely divided, inorganic particulate is included in the blast tube insulators in a range between 10—60 phr, preferably in a range between 15—50 phr. The inorganic filler preferably has a particle size of between 10 and 50 μ m (average diameter), and more preferably between 20 and 40 μ m in average diameter. The preferred inorganic filler is silica, particularly hydrated silica formed by precipitation. HiSil (registered trade mark) silica available from Harwick Chemical is the preferred inorganic particulate for use in insulators of this invention.

Other siliceous inorganic particulates can be used in accordance with this invention and include mica, glass, quartz and combinations thereof which may be used alone or together with the silica. Preferably, however, the inorganic particulate consists essentially of silica, particularly hydrated silica of the particle size identified above.

The polyaramide pulp suitable for use in this invention is commercially available, being sold for example, by E. I. duPont as Kevlar (registered trade mark) aramide pulp fiber. The polyaramide pulp preferably is a short, highly fibrillated fiber in which the fibrillation is resultant of axially oriented, strong crystallites that are less strongly bonded transversely. Fibrillation of the pulp fiber leads to length to

EP 0 172 957 B1

diameter ratios (L/D) of over 500. An important advantage of these polyaramide pulps is their very high decomposition temperatures ranging above about 400°C. In addition, these polyaramide pulps are low density and decompose into a strong, adherent char.

The preferred polyaramide pulps have physical properties as set forth in Table I:

TABLE I

Tensile strength MPa	3000—4000
Tensile modulus GPa	75—100
Elongation %	3—5
Density g/cc	1.4—1.5
Filament dia. μ m	10—14
Degradation temp.	400—600°C
Thermal expansion coefficient	$-2 \times 10^{-6}/^{\circ}\text{C}$

Further characterization of suitable polyaramide pulps currently available for use in this invention are set forth in Table II below:

TABLE II

	A*	B*	C*
+14 Mesh†	16±5%	4±2%	4±2%
-14+30 Mesh	22±5	17±3	17±3
-30+50 Mesh	25±3	33±5	33±5
-50+100 Mesh	19±4	26±2	26±2
-100 Mesh	17±5	20±4	20±4
Nominal average length	4 mm	2 mm	2 mm

* Kevlar (registered trade mark) pulps sold by Dupont as Long Wet Lap, Merge 6F204; Short Wet Lap Merge 6F205; and Dry Pulp Merge 6F218, respectively.

† U.S. Standard Sieve sizes.

The dry pulp C is preferred for this invention. Drying of the other pulps B and C prior to compounding enhances their utility for use in this invention. The above characterizations of suitable polyaramide pulps is for exemplification only; other similar aromatic polyamides including, for example, polyaramide fibers can be suitably employed in this invention.

The carbon fiber useful as the fibrous reinforcement of the insulating materials is commercially available. The length of the fiber is preferably between 2 and 10 millimeters, e.g. between 4 and 8 mm, with diameters between 4 and 16 microns. The carbon fiber can be made by heating polyacrylonitrile or pitch filaments for a time sufficient to reduce the fiber to highly carbonized form followed by chopping the filaments into desired form.

Exemplary characteristics for carbon fiber suitable for use in this invention and made from polyacrylonitrile precursor fiber are set forth below in Table III:

TABLE III

Tensile strength	2,480 MPa
Tensile modulus	206 GPa
Ultimate elongation	1.2%
Density	1.77 g/cm ³
Size content (% by weight)	7% max.
Bulk density	280 g/l
Filament diameter	8 microns
Filament shape	Round

The blast tube insulators of this invention can be made by blending the aforescribed ingredients in dry form followed by introducing the dry blend into a mold. However, use of a dry blend of particulate can result in ingredient separation during handling and storage. Accordingly, the preferred compounding procedure uses an initial dry blending of the insoluble ingredients followed by addition of the phenolic resin materials dissolved in solvent. Use of a vertical planetary mixer device is preferred for this compounding. The addition of dissolved phenolic resin materials to the admixed particles over the period of mixing permits the phenolic resin materials to deposit on the inorganic and organic particulates in the mixture. These particulates, carrying the plated out phenolic resin material, tend to agglomerate during

EP 0 172 957 B1

mixing into small clumps. It is preferred that the clumps or crumbs are kept within a particle size of between 4 and 8 millimeters.

Exemplary solvents for this mixing procedure are low boiling polar solvents such as methylethylketone, acetone, and ethyl alcohol. After the crumb is formed, it is tumbled in dry air (temperature e.g. 16—27°C to remove the solvent.

Curing of the blast tube insulators is under pressure (e.g. 500—2000 psig (3.48—13.79 MPa)) at temperatures ranging between 93 and 232°C. A preferred cure cycle is cure at a temperature of between 93 and 107°C for between 1—3 hours followed by cure at temperatures in a range between 149 and 204°C for 1—3 hours. The cured insulators are preferably cooled before release of pressure. The aforementioned dual heating procedure followed by cooling in the mold reduces the probability of cracking during molding of the insulators.

The blast tube insulators of this invention preferably have densities between 1.439 and 1.495 Mg/m³. This density is lower (e.g. 16%) than certain conventional phenolic blast tube insulators containing chopped carbon or silica cloth. The lower density coupled with comparable char rate performance leads to better insulators for the blast tubes.

Exemplary formulations A and B for the blast tube insulators of this invention are set forth in Table IV below (amounts are in parts by weight):

TABLE IV

Ingredient	Formulation A	Formulation B
Phenolic resin materials	100	100
Carbon fiber	40—120	—
Polyaramide pulp	—	40—120
Silica particulate	10—30	30—50

Certain preferred insulators of this invention have between 40 and 80 phr polyaramide pulp, between 10 and 30 phr of finely divided siliceous inorganic particulate and a density between 1.439 and 1.467 Mg/m³; or between 80 and 120 phr of carbon fibres, between 30 and 50 phr of finely divided siliceous inorganic particulate and a density between 1.467 and 1.495 Mg/m³; or between 40 and 80 phr of carbon fibres between 2 and 10 mm long and between 10 and 30 phr of finely divided siliceous inorganic particulate.

The following examples illustrate this invention but are not meant as a limitation thereof. In these examples, all parts are parts by weight unless specifically noted otherwise. As used in these examples, "Erosion Rate" is defined as the thickness of the insulator before test less the thickness after the test divided by action time where action time is the time between when the motor starts to exhaust at 7 kg/cm² and when the exhaust decreases to 7 kg/cm². "Chart Rate" is defined as the insulator thickness after the test minus the thickness after removal of char divided by the action time. "Decomposition Rate" is defined as the insulator thickness before the test minus the thickness after char removal divided by the action time. Erosion rate values derived from an accumulation rather than a removal of material during the test (such that the subtraction noted above would not lead to a positive number), are preceded by a plus (+) sign.

Example 1

Set forth in Table 1 below is a comparison between blast tube insulators of this invention (formulations A, B, C) and those of the prior art (D, E). As can be seen from data of this Table 1, the insulators of this invention can be lower in density and still have properties in two-inch (5.08 cm) rocket motor test firings that are comparable to those of insulators made from commercially-available material. All the insulators (A, B, C) of this invention in Table 1 were prepared by blending of the ingredients followed by molding at 10.34—13.79 MPa for 2—3 hours at about 177°C.

EP 0 172 957 B1

TABLE 1

	Ingredient, phr	A	B	C	D ^(a)	E ^(a)
5	Phenolic resin ^(b)	100.0	100.0	100.0		
	Hydrated silica, precipitated ^(c)	20.0	20.0	20.0		
	Carbon fiber (1.55 cm) ^(d)	50.0				
	Carbon fiber ^(e)		50.0			
	Polyaramide pulp ^(f)			100.0		
10	Silica cloth, chopped (1.27 cm sq)				400.0	
	Phenolic resin ^(g)				100.0	
	Phenolic resin ^(h)					100.0
	Carbon cloth, chopped (1.27 cm sq)					194.1
15	Erosion data & mass flux of approx. .13 kg/sec-cm ²⁽ⁱ⁾					
	Erosion rate, mm/sec	.051	.025	.038	+.152	.127
	Decomposition rate, mm/sec	.356	.114	.178	.737	.254
	Char rate, mm/sec	.279	.0762	.1397	.9144	.127
20	Density, mg/m ³	1.484	1.475	1.448	1.772	1.500

^(a) Product of Fiberite Co. MX2646; MX4926.

^(b) Resinox 755 product of Monsanto.

^(c) HiSil product of P.P.G. Industries.

25 ^(d) Magnamite 1810 as product of Hercules Incorporated, passed through roll mills.

^(e) Cellion C-6 product of Celanese.

^(f) Kevlar 29 pulp, type 979, merge 6F 218.

^(g) Polyamide modified phenolic resin.

^(h) Phenolic resin, MIL-R-9299, Type II.

30 ⁽ⁱ⁾ Data from two-inch (5.08 cm) motor firings.

The words "Resinox", "HiSil", "Magnamite" and "Kevlar" are understood to be registered trade marks.

35 As can be seen from the data on Table 1, the insulators of this invention (formulations A, B, C) have erosion, decomposition and char rates comparable to those of the prior art (formulations D, E). Since the density of the insulator of this invention is lower than the insulators made from commercially-available material, as can also be seen from Table 2, a smaller weight of insulation can be used, or a greater amount of low density insulation can be used to yield better performance at the same weight level.

40 Example 2

Set forth in Table 2 is a summary of data obtained in firing subscale rocket motors that were insulated in accordance with this invention (2A—2J) or with commercially-available material (MX2646, 4926). Table 3 shows the formulations of the blast tube insulators of Table 2. "Erosion Rate" and "Decomposition Rate" are defined as indicated above, as insulator thickness differences before and after testing divided by the action time, and erosion rate values derived from an accumulation rather than a removal of material during the test are preceded by a plus (+) sign.

As can be seen from Table 2 and 3, the blast tube insulators of this invention perform in a manner comparable to the insulators made of commercially-available material.

EP 0 172 957 B1

TABLE 2

5	Formulation No.	Decomposition rate mm/sec mass flux			Erosion rate mm/sec mass flux			Density* Mg/m ³
		Low	Med.	High	Low	Med.	High	
	2A	.457	.812	.889	+.102	+.102	.025	1.520
	2B	.381	.610	.660	.025	.025	.025	1.448
	2C	.305	.584	.584	+.711	+.025	.076	1.140
10	MX-2646	.381	.457	.533	+.381	+.381	+.229	1.772
	2D	.381	.635	.711	+.737	+.102	.025	1.475
	2E	.330	.813	.838	+.330	+.076	.051	1.575
	2F	.330	.635	.787	+.203	+.025	.279	1.276
	MX-4926	.356	.686	.914	+.178	.025	.102	1.500
15	2G	.381	.508	.559	.076	.178	.229	1.357
	2H	.330	.559	.584	.051	.178	.203	1.390
	2O	.203	.559	.660	.127	.305	.508	1.413
	2J	.914	1.17	1.29	.102	.102	.178	1.672

20 * Theoretical

TABLE 3
Phenolic insulations

25	Ingredients, phr						
		2D	2A	2E	XO2646	MX4926	2B
	Phenolic resin ¹	100.0	100.0	100.0	—	—	100.0
	Silica ²	20.0	26.67	40.0	—	—	40.0
	Graphite fiber ³	50.0	—	—	—	—	—
	Graphite fiber ⁴	—	66.67	100.0	—	—	—
30	Phenolic resin (Mil-R-9299, Type II)	—	—	—	100.0 ⁽⁵⁾	100.0	—
	Silica cloth, chopped, 1.27 cm sq	—	—	—	400.0	—	—
	Carbon cloth, chopped 1.27 cm sq	—	—	—	—	194.1	—
	Polyaramide pulp ⁶	—	—	—	—	—	100.0

35 Phenolic-elastomeric insulations

40		2F	2C	2G	2H	2J	2K
	Chlorosulfonated polyethylene ⁷	80.0	50.0	100.0	100.0	100.0	100.0
	Liquid polybutadiene ⁸	20.0	30.0	—	—	—	—
	Polyisoprene ⁹	—	20.0	—	—	—	—
	Polyaramide pulp ⁶	50.0	50.0	200.0	1250.0	2500.0	—
	Starch	40.0	40.0	40.0	40.0	40.0	40.0
	Magnesia	6.0	2.0	6.0	6.0	6.0	6.0
45	Sulfur accelerator ¹⁰	2.0	1.0	2.0	2.0	1.0	1.0
	Phenolic resin ¹	100.0	100.0	200.0	500.0	500.0	500.0
	Peroxy curative ¹¹	—	3.75	—	—	—	—
	Silica ²	—	—	40.0	—	—	—
	Graphite fiber ³	—	—	—	—	—	2500.0

¹ Resinox 755, Monsanto.

² HiSil, Harwick.

³ Celion 6, Celanese.

⁴ Magnamite, Hercules.

55 ⁵ Polyamide modified.

⁶ Kevlar 29, DuPont.

⁷ Hypalon LP 999, DuPont.

⁸ Ricon 150, Colorado Speciality.

⁹ Natsyn 2200.

60 ¹⁰ Dipentamethyl nethiuriumhexasulfide, DuPont.

¹¹ 2,5-Dimethyl-2,5-di(t-butylperoxy)h xane.

The words "Resinox", "HiSil", "Magnamite" and "Kevlar" are understood to be registered trade marks. It is not known whether the trade names "Celion", "Hypalon", "Ricon" and "Natsyn" are registered trade marks.

EP 0 172 957 B1

Example 3

Eighteen-kilogram rocket motors were fabricated for testing the blast tube insulators of the invention. The formulations tested were 2B, 2C and 2D of Example 2, Tables 2 and 3.

Billets of these formulations 2B, 2C and 2D were molded. Two billets of each were required for testing: 2.5 inch (6.35 cm) outside diameter by 5 inch (12.7 cm) long, and 6.6 inch (16.76 cm) outside diameter by 2.5 inch (6.35 cm) long. These billets were compression molded in piston-type molds, then cured at 177°C. Blast tube insulator components were machined from the billets and bonded into the blast tube hardware, including ramp section.

The results of firing eighteen-kilogram motors containing these insulators are shown in Table 4. These results are for four motor firings, 1—4, and show Erosion rate (ER) and Decomposition rate (DR).

As can be seen by the results in Table 4, the insulation of this invention performed favorably.

TABLE 4

15	Location/ Motor No.	Mass flux velocity		2C		2B		2D	
		kg/sec-cm ²	m/sec	ER	DR	ER	DR	ER	DR
20	Ramp section								
	Motor No. 1	.0392	.296	.18	.18				
		.0492	36.9	.23	.15				
	Motor No. 2	.0372	31.7	.15	.13				
		.0475	40.2	.15	.15				
25	Blast tube								
	Motor No. 2	.0584	44.2	.30	.15				
		.1561	118	1.1	1.2				
		.4633	370	2.3	2.3				
30	Motor No. 3	.0555	47.2			.10	.18		
		.1687	145		.08	.33			
		.5062	472			1.3	1.4		
	Motor No. 4	.0541	47.9					0	.63
		.1659	147					.13	.66
		.5941	611					.30	.91

Claims

1. A rigid molded insulator suitable for thermally shielding the blast tube of a rocket motor and formed from a cured phenolic resin composition containing fibrous reinforcement material, characterized in that the fibrous reinforcement material is dispersed in the resin composition and comprises polyaramide pulp or carbon fibers or a combination of said pulp and fibers, and in that for each 100 parts by weight of phenolic resin the insulator contains between 30 and 120 parts by weight of the said reinforcement material and between 10 and 60 parts by weight of a finely divided siliceous inorganic particulate, the insulator having a density between 1.14 and 1.495 Mg/m³.

2. A rigid molded insulator as claimed in claim 1, characterized in that it contains between 40 and 80 parts by weight of polyaramide pulp and between 10 and 30 parts by weight of finely divided siliceous inorganic particulate, per hundred parts by weight of the phenolic resin, the insulator having a density between 1.439 and 1.467 Mg/m³.

3. A rigid molded insulator as claimed in claim 1, characterized in that it contains between 80 and 120 parts by weight of carbon fibers and between 30 and 50 parts by weight of finely divided siliceous inorganic particulate, per hundred parts by weight of the phenolic resin, the insulator having a density between 1.467 and 1.495 Mg/m³.

4. A rigid molded insulator as claimed in claim 1, characterized in that it contains between 40 and 80 parts by weight of carbon fibers that are between 2 and 10 millimeters long, and between 10 and 30 parts by weight of a finely divided siliceous inorganic particulate, per hundred parts by weight of the phenolic resin.

5. A rigid molded insulator as claimed in claim 4, characterized in that the carbon fibres are between 4 and 8 millimeters long.

6. A rigid molded insulator as claimed in claim 1, 4 or 5 characterized by a density between 1.439 and 1.495 Mg/m³.

7. A rigid molded insulator as claimed in any of the preceding claims, characterized in that the phenolic resin composition contains up to 100 parts by weight of a cross-linked elastomeric polymer per hundred parts by weight of the phenolic resin.

8. A rigid molded insulator as claimed in any of the preceding claims, characterized in that the finely divided inorganic particulate comprises silica.

9. A method of preparing the blast tube insulator as claimed in claim 1, 4 or 8, characterized in that a

EP 0 172 957 B1

curable precursor for the cured phenolic resin is admixed with the finely divided, siliceous inorganic particulate and the fibrous reinforcement in the presence of a solvent for the precursor until a molding crumb having a diameter between 4 and 8 millimeters results, the crumb is dried by tumbling in dry air and loaded into a mold, and sufficient pressure to consolidate the crumb is applied to the crumb in the mold at a temperature between 93 and 232°C for a time sufficient to cure the precursor and form the insulator.

Patentansprüche

1. Steifer, geformter Isolator, der zum thermischen Schutz der Raketenbrennkammer geeignet ist und aus einer gehärteten Phenolharzzusammensetzung, die faseriges Verstärkungsmaterial enthält, gebildet ist, dadurch gekennzeichnet, daß das faserige Verstärkungsmaterial in der Harzzusammensetzung dispergiert ist, und Polyaramid-Pulpe oder Kohlenstoffasern oder eine Kombination dieser Pulpe und der Fasern enthält, und dadurch, daß pro jeweils 100 Gewichtsteile Phenolharz der Isolator zwischen 30 und 120 Gewichtsteile des Verstärkungsmaterials und zwischen 10 und 60 Gewichtsteile eines fein zerteilten, siliziumhaltigen, anorganischen, aus Partikeln bestehenden Stoffes, enthält, wobei der Isolator eine Dichte zwischen 1,14 und 1,495 Mg/m³ aufweist.

2. Steifer, geformter Isolator nach Anspruch 1, dadurch gekennzeichnet, daß er zwischen 40 und 80 Gewichtsteile Polyaramid-Pulpe und zwischen 10 und 30 Gewichtsteile fein zerteilten, siliziumhaltigen, anorganischen, aus Partikeln bestehenden Stoff pro hundert Gewichtsteile des Phenolharzes enthält, wobei der Isolator eine Dichte zwischen 1,439 und 1,467 Mg/m³ aufweist.

3. Steifer, geformter Isolator nach Anspruch 1, dadurch gekennzeichnet, daß er zwischen 80 und 120 Gewichtsteile Kohlenstoffasern und zwischen 30 und 50 Gewichtsteile fein zerteilten, siliziumhaltigen, anorganischen, aus Partikeln bestehenden Stoff pro hundert Gewichtsteile des Phenolharzes enthält, wobei der Isolator eine Dichte zwischen 1,467 und 1,495 Mg/m³ aufweist.

4. Steifer, geformter Isolator nach Anspruch 1, dadurch gekennzeichnet, daß er zwischen 40 und 80 Gewichtsteile Kohlenstoffasern mit einer Länge zwischen 2 und 10 Millimetern und zwischen 10 und 30 Gewichtsteile fein zerteilten, siliziumhaltigen, anorganischen, aus Partikeln bestehenden Stoff pro hundert Gewichtsteile des Phenolharzes enthält.

5. Steifer, geformter Isolator nach Anspruch 4, dadurch gekennzeichnet, daß die Kohlenstoffasern zwischen 4 und 8 Millimeter lang sind.

6. Steifer, geformter Isolator nach Anspruch 1, 4 oder 5, gekennzeichnet durch eine Dichte zwischen 1,439 und 1,495 Mg/m³.

7. Steifer, geformter Isolator nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Phenolharzzusammensetzung bis zu 100 Gewichtsteile eines quervernetzten elastomeren Polymers pro hundert Gewichtsteile des Phenolharzes enthält.

8. Steifer, geformter Isolator nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der fein zerteilte, anorganische aus Partikeln bestehende Stoff Kieselsäureanhydrid umfaßt.

9. Verfahren zur Herstellung des Brennkammer-Isolators nach Anspruch 1, 4 oder 8, dadurch gekennzeichnet, daß ein härthbarer Vorläufer für das gehärtete Phenolharz dem fein zerteilten, siliziumhaltigen, anorganischen, aus Partikeln bestehenden Stoff und dem faserigen Verstärkungsmittel in Anwesenheit eines Lösungsmittels für den Vorläufer beigemischt wird, bis ein Formkrümel mit einem Durchmesser zwischen 4 und 8 mm entsteht, der Krümel in trockener Luft durch Trommeln getrocknet und in eine Form geladen wird und, ausreichend Druck zur Verfestigung des Krümel auf den Krümel in der Form bei einer Temperatur zwischen 93 und 232°C für eine Zeit, die ausreichend ist, um den Vorläufer zu härten und den Isolator zu bilden, angewandt wird.

Revendications

1. Isolateur moulé rigide, convenant comme écran thermique pour la tuyère d'un moteur-fusée et formé en une composition de résine phénolique durcie contenant une matière fibreuse de renfort, caractérisé en ce que la matière fibreuse de renfort est dispersée dans la composition de résine et est faite de pulpe de polyaramide ou de fibres de carbone, et en ce que pour 100 parties en poids de résine phénolique, l'isolateur contient entre 30 et 120 parties en poids de ladite matière de renfort et entre 10 et 60 parties en poids d'une matière inorganique siliceuse particulaire finement divisée, l'isolateur ayant une masse volumique comprise entre 1,14 et 1,495 Mg/m³.

2. Isolateur moulé rigide selon la revendication 1, caractérisé en ce qu'il contient entre 40 et 80 parties en poids de pulpe de polyaramide et entre 10 et 30 parties en poids de matière inorganique siliceuse particulaire finement divisée pour 100 parties en poids de la résine phénolique, l'isolateur ayant une masse volumique comprise entre 1,439 et 1,467 Mg/m³.

3. Isolateur moulé rigide selon la revendication 1, caractérisé en ce qu'il contient entre 80 et 120 parties en poids de fibres de carbone et entre 30 et 50 parties en poids de matière inorganique siliceuse particulaire finement divisée pour 100 parties en poids de la résine phénolique, l'isolateur ayant une masse volumique comprise entre 1,467 et 1,495 Mg/m³.

4. Isolateur moulé rigide selon la revendication 1, caractérisé en ce qu'il contient entre 40 et 80 parties en poids de fibres de carbone dont la longueur est comprise entre 2 et 10 mm et entre 10 et 30 parties en

EP 0 172 957 B1

poids d'une matière inorganique siliceuse particulière finement divisée, pour 100 parties en poids de la résine phénolique.

5. Isolateur moulé rigide selon la revendication 4, caractérisé en ce que les fibres de carbone ont une longueur comprise entre 4 et 8 mm.

6. Isolateur moulé rigide selon l'une quelconque des revendications 1, 4 et 5, caractérisé par une masse volumique comprise entre 1,439 et 1,495 Mg/m³.

7. Isolateur moulé rigide selon l'une quelconque des revendications 1 à 6, caractérisé en ce que la composition de résine phénolique contient jusqu'à 100 parties en poids d'un polymère élastomère réticulé pour 100 parties en poids de la résine phénolique.

8. Isolateur moulé rigide selon l'une quelconque des revendications 1 à 7, caractérisé en ce que la matière inorganique particulière finement divisée comprend de la silice.

9. Procédé de préparation de l'isolateur pour tuyère selon l'une quelconque des revendications 1, 4 et 8, caractérisé en ce qu'un précurseur durcissable de la résinephénolique durcie est mélangé avec la matière inorganique siliceuse particulière finement divisée et la matière fibreuse de renfort en présence d'un solvant pour le précurseur, jusqu'à ce qu'il en résulte un granulé de moulage ayant un diamètre entre 4 et 8 mm, le granulé est séché par tonnelage dans l'air sec et chargé dans un moule, et une pression suffisante pour compacter le granulé est appliquée à celui-ci dans le moule à une température comprise entre 93 et 232°C pendant un temps suffisant pour durcir le précurseur et former l'isolateur.

20

25

30

35

40

45

50

55

60

65